Conference report

Perspectives on GOLD 2009

The 5th International Conference on the Science, Technology and Applications of Gold took place during 26th – 29th July, in Heidelberg, Germany. The following are a selection of personal viewpoints and highlights from some of the participants.

Christopher Corti, Chairman, GOLD 2009

The 5th gold conference was co-organised by World Gold Council and the University of Heidelberg and attracted a record attendance of over 350 delegates from 40 countries worldwide. There was a notable strong contingent of students, many of whom presented posters on their research. There was a stronger emphasis on applications-oriented presentations and, in support, the conference also featured some trade stands, including Gold Bulletin, Metalor, Allegemeine, Project AuTEK, Strem Chemicals (who market a range of gold catalysts including those produced by Project AuTEK in South Africa), but perhaps the highlight was the stand by 3M Inc who exhibited their range of commercial applications for gold catalysts.

As has become traditional, the conference comprised 4 parallel sessions, and on some days, this expanded to 5 sessions to cope with all the presentations. Coupled with this, two poster sessions were held to showcase the many posters on the latest research results on a wide range of topics – catalysis, chemistry, nanotechnology, biomedical, materials and more besides.

The conference commenced on Sunday afternoon with 3 invited Plenary Lectures. Peter Kondos (Barrick Gold, Canada) who gave delegates an insight into "An overview of modern gold mining", with a look at the some of the issues that face the gold mining industry. This was followed by Christian Hagelüken (Umicore, Germany) who spoke about "Recycling of gold from electronics", showing how an integrated approach to recovery of metals is necessary. The last presenter was Christiane Eluère (Musee de France, Paris) who entranced us with her talk on "The earliest story of gold and goldwork in continental Europe", showing many examples of early gold artifacts found in excavations around Europe. The quality of manual craftsmanship by early man is truly awe-inspiring.

An active member of the Organising and Catalysis committees of all the recent gold conferences, David Thompson, unfortunately died a few weeks before the conference, following a serious illness. As a mark of his contribution and esteem, a 'David Thompson Memorial Lecture' was instigated and the first was presented by Jeroen van Bokhoven of the ETH in Zurich, who spoke on the "Catalytically active species in gold catalysts".

Two student prizes were awarded. Well, 3 actually as the judges tied on their decision for the *Best Oral Presentation*, which went to Telisha Traut (University of Johannesburg) and Jonathan Edgar (University of Technology Sydney), whilst the prize for the *Best Poster* went to Nadine Meyer, University of Wuppertal. They each receive a book of their choice. Congratulations to all three; the competition was very strong!

In summary, this was an excellent conference; the quality of presentations was high, the weather held and the organisation was superb. The feedback from delegates was good. The 6th Gold conference, GOLD 2012, is probably to be held in Asia. An announcement will be made in a later issue of Gold Bulletin.

Geoffrey Bond, UK

At GOLD 2009 contributions on gold catalysis (my personal interest) were given in Plenary and Invited Lectures, and in two parallel sessions of oral presentations, as well as in two poster sessions. The lack of requirement to produce full texts appeared to encourage repetition of work already published, and it is unclear where new work will eventually be seen in print. The following review is therefore based on the book of Abstracts and on notes taken at the talks I was able to attend. Constraint on length forbids the quoting of the names and addresses of all authors whose work deserves to be cited; instead the page number in the Abstract book is used as reference. For those not having access to this book or its CD, names and addresses can be obtained either at the Gold Bulletin website or from the editor or myself.

A few general remarks on the work presented are in order. There was continued emphasis on experimental observations, with little attention to theory or mechanisms; most of the work had distinct and immediate practical objectives. It was disappointing to see that a number of authors still regard recording a conversion-temperature plot as an adequate expression of activity, and in the case of CO oxidation the lack of measurements at sub-ambient temperatures sometimes limited the significance of the work. This reaction continues to attract attention, and is still the first choice for assessing the activity of a new catalyst; some 24 contributions were made on this reaction, the emphasis turning from activity to long-term stability. There is a rapidly growing interest in the oxidation of organic molecules (42 contributions), the stress being on getting the desired product with high selectivity. There was comparatively little interest in the Water-Gas Shift or in selective oxidation of CO (PROX), and somewhat surprisingly almost nothing on H_2O_2 synthesis except from the Cardiff group. Some new reactions and applications deserve mention (see below); there was also evidence of rapid growth in the use of gold cations and complexes for catalysing organic reactions, but these are not covered in this

report. The general impression created by the work presented at GOLD 2009 was of attention to new catalyst compositions and supports, and to new preparation methods. Some of the more interesting and useful of these are mentioned below.

Oxidation of carbon monoxide

Little attention has been paid to bimetallic catalysts for this reaction, but the addition of nickel (78) or of iridium (392) to gold was shown to be beneficial. The inclusion of other oxides (e.g. In_2O_3 with Au/TiO_2 (289), rare earth oxides with Au/CeO_2 (291) and Au/TiO_2 (313), CeO_2 and TiO_2 with Au/SiO_2 (185), CoO with Au/SiO_2 (173)) is also generally helpful. Unusual supports that have been tested include H-mordenite (184), hollow ZrO_2 spheres in which gold particles are encapsulated (123), mesoporous TiO_2 (331) and perovskites (304). A novel concept involves incorporating the reductant (citrate ion) into the support (307).

Variations to the procedures for preparation and pre-treatment have been explored. Increasing the air flow during drying the precursor to Au/TiO_2(rutile) decreases the gold particle size (171), and alteration to the morphology of CeO_2 (175) and ZrO_2 (306) affects activity. Pre-treatment of a TiO_2 support at high pH enhances the concentration of strongly held OH groups, to the benefit of activity (151), and large inactive gold particles can be removed from an Au/TiO_2 catalyst by cyanide treatment (284). Loss of activity during storage is accompanied by removal of OH groups, and is minimised when samples are refrigerated (187).

Au/TiO_2 and Au/ZrO_2 have been employed as cigarette filters to remove CO, but particulates in smoke cause activity loss (120). Supported gold catalysts offer a practical alternative to Hopcalite in respiratory devices (189), and gold in combination with platinum group metals (Pt, Pd) is destined to find used in treating automotive (121) and diesel (148) exhaust.

Oxidation of organic molecules

It is now well established that gold catalysts, either supported or unsupported, are active and selective for the oxidation of alcohols, polyols and aldehydes, using either air, O_2 or H_2O_2 as oxidant (183, 299); commonly used molecules for testing formulations and procedures are glycerol, benzyl alcohol and D-glucose. The action of gold is frequently enhanced by its admixture with palladium, although the reasons for this are unclear. Ten contributions to the conference bear witness to the continuing interest in gold for catalysing the epoxidation of alkenes.

It is evident that the course of reaction followed and the products formed depend critically on the conditions employed. Thus for example D-glucose is oxidised to D-gluconic acid on Au/Al_2O_3 (299, 300) (i.e. –CHO to –COOH), and other aldoses to the corresponding aldonic acids (142), while Au/C catalyses its oxidation by O_2 to the C_3 compound tartronic acid or by H_2O_2 to the C_2 compound glycolic acid (183). A method for making Al_2O_3 spheres with an egg-shell coating of gold was reported (190), and other novel supports for gold and gold + palladium include polyaniline (286), carbon nanotubes (91), porous coordination polymers (89), and SiO_2-encapsulated Fe_3O_4 (324), which enables the catalyst to be recovered magnetically. A silver-gold colloid (Ag:Au = 1:4) is 18 times more active than gold alone for glucose oxidation. Aqueous ethanol can be selectively oxidised to acetic acid at 423 K over Au/TiO_2 (73) or above 473 K to CO_2 and water (76). Methanol oxidation also follows alternative paths: on Au/Al_2O_3 promoted by CeO_2 and ZrO_2, formaldehyde (methanal) is formed (203), while on nanoporous gold the product is methyl formate. Deep oxidation leads to CO_2 and water via the decomposition products of dimethylether formed by dehydration.

Various gold catalysts will oxidise propene to propene oxide (methyloxirane) selectively at low conversions, so the search is on for catalysts that retain acceptable selectivity at higher conversions, i.e. which are less active for the further oxidation of the epoxide. Gold supported on sodium-treated TS-1 (titanosilicate) affords 7.3% conversion at 85% selectivity (93), and works equally well with either water or H_2+O_2. AuCo/TS-1 shows good stability, the cobalt assisting the reaction of H_2+O_2 (303). H_2O_2 is a by-product of the oxidation of CO under aqueous conditions, and can be used for the simultaneous epoxidation of butene with Au/TiO_2 or Au/TS-1 (394). A transient kinetic study of the reaction over Au/TiO_2 reveals a two-step formation of CO_2 (92). Very small gold clusters (6-10 atoms) on Al_2O_3 give propene oxide when water is present, but acrolein (propenal) in its absence (208). Styrene forms the epoxide and benzaldehyde with Au_{55}/SiO_2 as catalyst (136), while cyclohexene gives mainly the decomposition products of the epoxide (94).

Deep oxidation of propene takes place above 473 K on various supported gold catalysts (208, 292,339).

Hydrogenation

Previous work showing the ability of gold catalysts to hydrogenate ethyne and butadiene selectively to the corresponding alkenes has been amply confirmed. Au/CeO_2 performs well for ethyne hydrogenation above 473 K (140), and Au/Al_2O_3 promoted by ceria and other basic oxides is also satisfactory, although deactivation remains a problem (79). Small amounts of palladium added to Au/Al_2O_3 accelerate the hydrogenation of butadiene without lowering selectivity (139, 391), and also assists the selective hydrogenation of p-chloronitrobenzene to the amine (138). αβ-Unsaturated ketones are reduced to the corresponding alcohols in the presence of Au/CeO_2 (170).

Preparation of pure hydrogen

This is achieved either by the Water-Gas Shift (WGS) or by the selective oxidation of CO impurity in H_2 (PROX). With WGS, variation of the Ce:Zr ratio in the CeO_2-ZrO_2 support had little effect (217), but with Au/ZrO_2 conversion increases with the area of the support and as the particle size of the gold gets

smaller (293). Activity now appears to be due to very small clusters of Au^0 (108), and deactivation to its reduction to $Au^{\delta-}$ (109). Au/TiO_2 performs better than $CuZn/Al_2O_3$ (107), so there remains some prospect of large-scale application. For PROX, $Au@CeO_2$ (gold embedded in CeO_2) is stabler than Au/CeO_2 made by DP (309), and activity loss is associated in part with the loss of available oxygen from the support (214).

Other reactions

The steam-reforming of methanol

$$CH_3OH + H_2O \rightarrow 3H_2 + CO_2$$

is accomplished with high conversion over Au/Fe_2O_3-CeO_2 at 623 K (312), and its carbonylation

$$CH_3OH + CO \rightarrow CH_3COOH$$

by Au/C in the presence of iodine; very small clusters of gold are the active species (152). Methyl-tert-butylether (MTBE) in water is decomposed photochemically over TiO_2 with visible light, the process being accelerated by small gold particles (d <7.5 nm) on the TiO_2 (290).

Structure of the metal-support interface

Developments in techniques for structural characterisation now permit observing the metal-support interface in astonishing detail. Use of high-angle annular dark-field scanning transmission electron microscopy (HAADFD-STEM) has revealed the structure of the Au/CeO_2 interface, at which the gold is disordered (194); changes in the structure have been examined by first-principles studies of Au/CeO_2(111) (314) and Au/TiO_2(110) (205). High-energy resolution fluorescence-detected X-ray spectroscopy (HERFD-XRS) allows the oxidation state and particle size of gold to be determined under reaction conditions, activity for CO oxidation being ascribed to Au^0 species (206). Modification of the TiO_2 surface by basic promoters and OH groups has been modelled by molecular dynamics simulation (320).

Conclusion

The work on gold catalysis fully demonstrates the continued growth of interest in what this metal can achieve; problems of stability are being overcome, and significant large-scale applications appear imminent. These would have pleased David Thompson had he been spared to witness them. The astronomic increase in the relevant literature has astounded but delighted the pioneers of this new field of catalysis.

Trevor Keel, Project Manager, World Gold Council

Gold nanoparticle research is booming, a statement proved by the various nano-focused symposia on offer at GOLD2009. The range and depth of science was superb, both from the oral presentations and poster sessions.

There were a number of symposia focusing on the biosensing and biomedicine arenas. Vince Rotello (Keynote) and Qun Huo gave excellent talks on the use of gold nanoparticles in diagnostic applications, followed by a presentation from Christophe Alric detailing his efforts on the design of gold nanoparticles for in vivo imaging and X-ray therapy. The idea of harnessing gold nanoparticulates as potential therapeutic vehicles was continued with talks from Ramya Jagannathan, Cleo Dodgen and Ndabenhle Sosibo, all of whom detailed the potential of functionalised nano-gold to be used in the treatment of diseases such as Alzheimers, HIV and cancer. In fact the therapeutic uses of gold were a popular subject with Luigi Messori (Keynote), Telisha Traut (joint student prize winner) and Thomas Fassler all presenting their work on the synthesis and biomedical applications of gold compounds. Finally Michael Wilson and Vladamir Zaporojtchenko both impressed with their presentations discussing the use of gold nanoparticles in light-activated antimicrobial agents.

I was particularly excited to see the sheer diversity of novel applications of gold nanoparticle technology. Optical properties are a big part of this, with excellent talks from Cyrille Gautier on doping plastics with gold nanorods and Jim Johnson discussing his work in colouring textiles with nano-gold. Mike Cortie then spoke eloquently about the vast industrial potential of spectrally selective window coatings employing gold nanorods. Michael Natan from Oxonica described the development of biochemical detection & anti-counterfeiting methods using gold nanoparticle SERS. Other highlights included Mikael Kall's Keynote address discussing the use of gold nanostructures for efficient refractive index sensing, and Janina Kneipp's talk on gold nanosensors based on one- and two-photon SERS.

The final main area of research concerned the synthesis and properties of gold nanoparticles and gold-containing compounds. Didier Astruc delivered an excellent Keynote discussing the interplay between gold nanoparticles and dendrimers. Julien Bouden then discussed liquid-crystalline gold nanoparticles, and Laura Ashfield from Johnson-Matthey presented her work on tools to enhance understanding of gold nanoparticle synthesis. Other highlights included Jonathan Edgar (joint student prize winner) discussing the synthesis of highly anisotropic gold nanoparticles, and Danny Leznoff's excellent introduction to highly birefringent cyanoaurate-based coordination polymers.

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